



Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

THE ACTION OF ETHYL CHLORSULFONATE UPON ANILINE.

By F. W. BUSHONG, Kansas City University, Kansas City, Kan.

Read before the Academy, at Topeka, December 31, 1904.

A STUDY of the action of sulfuryl chloride and of ethyl chlor-sulfonate upon aniline, dimethylaniline and acetanilide was first undertaken by Wenghoffer,¹ who drew the following conclusions from the results of his experiments:

I. By the action of sulfuryl chloride upon aniline and upon anilides chlorine substitution products are obtained.

By the action of ethyl chlorsulfonate upon these bodies, products are formed which contain the $\text{—SO}_2\text{OH}$ group, bound directly to the benzene nucleus. With aniline, for example, he obtained sulfanilic acid.

J. Wagner² prepared a body from pyridine and chlorsulfonic acid which had the composition $\text{C}_5\text{H}_5\text{NSO}_3$, and which, with water or alcohol, decomposed, forming pyridine sulfate and sulfuric acid, or ethylsulfuric acid, respectively; and found that on dissolving it in aniline and adding ether, crystals of the aniline salt of phenylsulfaminic acid separate. He pointed out that Wenghoffer probably overlooked this salt, owing to the fact that he treated his crude reaction product with water.

W. Traube³ isolated salts of aromatic sulfaminic acids, which he obtained by treating aromatic amines with chlorsulfonic acid, and Bamberger⁴ has studied the transformation of phenylsulfaminic acid into sulfanilic acid.

It seemed desirable, therefore, to again take up the study of the action of ethyl chlorsulfonate upon aniline.

Ethyl chlorsulfonate (1 mol.) was dropped into an ice-cold ligroin solution of aniline (3 mols.) Each drop instantly produced a white crystalline precipitate. The crystals were thrown upon a filter and washed, first with ligroin, afterwards with absolute ether. The ligroin solution was found to contain ethyl aniline, which was identified by converting it into ethylphenylnitrosamine. No trace of an ester could be found in either the ligroin or ethereal solution. A portion of the crystalline precipitate, heated to 150° , gave off vapors re-

1. J. prakt. Chem., (2), 16, 448 (1877).

2. Ber. d. chem. Ges., 19, 1157 (1886).

3. Ber. d. chem. Ges., 23, 1653 (1890).

4. Ber. d. chem. Ges., 30, 2275 (1897).

sembling aniline, a property described by Laar⁵ as belonging to the aniline salt of sulfanilic acid; although this salt was formed from the corresponding salt of phenylsulfaminic acid by heating, as the following work will show:

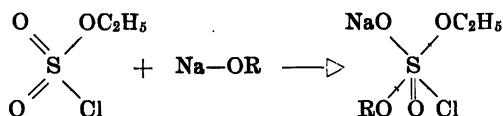
The crystalline precipitate, from which all free aniline and alkylated aniline had been removed, was treated with a solution of caustic potash, yielding an oil which was diazotized. No crystals of *p*-nitrosodiethylaniline were observed, but ethylphenylnitrosamine was obtained. The alkaline solution, which had been freed from aniline and alkylated aniline contained as a base in the salt, was acidified with hydrochloric acid and boiled about fifteen minutes. After cooling it was neutralized with caustic soda, and yielded aniline, which was converted into diazo-amido-benzene.

These experiments prove two points:

I. Aniline is alkylated by ethyl chlorsulfonate.

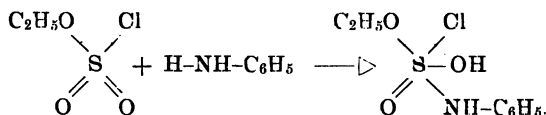
II. The ethylaniline salt of phenylsulfaminic acid is formed.

I have previously shown⁶ that while sulfuryl chloride dissociates readily into SO₂ and Cl₂, forming with sodium alcoholates large quantities of sodium sulfite, ethyl chlorsulfonate does not thus dissociate, but unites quantitatively with sodium alcoholates to form addition products, thus:



which may be broken down in one way (by water), forming RO—SO₂—OC₂H₅+NaCl, and also in another way (by heat), forming NaO—SO₂—OR+C₂H₅Cl, no sulfite whatever being formed.

It is, therefore, quite evident that both sulfuryl chloride and ethyl chlorsulfonate behave in a perfectly analogous manner toward aniline; *i. e.*, sulfuryl chloride dissociates and acts upon aniline as a chlorinating agent, while ethyl chlorsulfonate is not dissociated, but reacts additively, thus:

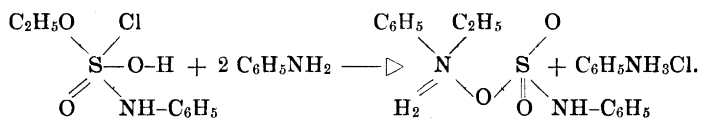


This addition product then reacts further with aniline, in a man-

5. J. prakt. Chem., (2), 20, 249 (1879).

6. Amer. Chem. Jour., XXX, 212-224 (1903).

ner analogous to that observed by Claesson and Lundvall,⁷ in the case of the alkyl sulfates, forming a product which yields by loss of hydrochloric acid the ethylaniline salt of phenylsulfaminic acid:



7. Ber. d. chem. Ges., 13, 1703. Cf. Ullmann und Wenner, Ibid., 33, 2476 (1900).